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CORNELL AERONAUTICAL LABORATORY, INC.
BUFFALO, NEW YORK 14221

CHORD WORKING PAPER

NO. 20

PREPARATIVE PHASE OF THE AGENT CS SLURRY INVESTIGATION

CONTRACT NO. DA-18-108-CML-6628(A)

Prepared By:

C.J. SCHNEIDER, JR.

DECEMBER 1964

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PREPARATIVE PHASE OF THE AGENT CS SLURRY INVESTIGATION

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Prepared by:

C. J. Schneider, Jr.

December 1964

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Weapons Development and Engineering Laboratories
Ground Munitions Laboratory
Edgewood Arsenal, Maryland 21010

Contract No. DA-18-108-CML-6628(A)
Project No. 4C04-15-029

Cornell Aeronautical Laboratory, Inc.
Buffalo, New York 14221

FOREWORD

The work described in this report was authorized under Project 4C04-15-029, Chemical Agent Dissemination Research (U).

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I. ABSTRACT

This paper covers the preparative phase of the investigation conducted by Cornell Aeronautical Laboratory into the dispersion of agent CS in slurries with characteristics useful in dissemination devices. Included are the results of the brief consideration given to the following items:

1. Choice of carrier liquid
2. Surfactant hydrophile and lipophile balance
3. Surfactant concentration
4. Agent concentration
5. The use of a protective colloid
6. The dissemination of slurries

The conclusion is reached that it is possible to prepare useful slurries containing high concentrations of agent CS and that these slurries possibly offer dissemination advantages. It is also conjectured that it should be possible by a similar investigation to develop a technique for the preparation of slurries of most other solid agents.

II. BACKGROUND

Cornell Aeronautical Laboratory, Inc. (CAL) originally undertook a brief study of dispersion techniques in an effort to generally broaden the adaptability of liquid dissemination systems, such as the high-pressure system or velocity generator system, for the candidate B-FLAT* munition by making these systems capable of handling present and future agents in the solid physical state.

A number of advantages to disseminating solids in preground slurry form are immediately evident. Among them are:

1. Ability to achieve better solid transport within disseminators. Slurries can be pumped, piped, moved by pressure, etc.
2. High packing density (greater volumetric efficiencies can frequently be obtained in slurries than even in highly compressed dry solids through the elimination of microscopic bridging which opposes compaction).
3. Ability to disseminate solids of extremely low volatility which the present pyrotechnic methods cannot handle without destructive temperature extremes.
4. Potential to improve coupling efficiency between energy source and material to be disseminated (a basic criterion of any dissemination system).
5. Potential protection of thermally delicate solids through evaporative cooling of particles. This effect may also reduce thermal pluming.

CAL began consideration of slurry techniques using saccharin as a simulant as suggested by CRDL. After a brief evaluation which indicated that:

*Refer to "Summary Report (U)," CAL Report No. GM-1592-G-23, Secret, for additional information on the B-FLAT munition.

(1) cyclohexane was a satisfactory carrier liquid (from the standpoint of crystal growth and handling ease);

(2) a surfactant HLB of 10.0 allowed the preparation of high concentration slurries of saccharin; and

(3) the use of lecithin as a protective colloid improved rheological properties and stability;

pourable slurries were prepared containing up to 70% saccharin by weight. These dispersions, at 50% and 70% solids by weight, and mass median diameters (mmd) between 5 and 10 microns, were successfully sprayed in a vertical wind tunnel through a 0.007-inch orifice fan spray nozzle at 5700 psi applied pressure. Cascade impactor samples from the spray compared favorably in particle size distribution with liquid sprayed under similar conditions. The amount of agglomeration was small, indicating that further work in the area would be fruitful.

Accordingly, CRDL suggested that CAL briefly conduct an investigation of dispersion techniques for agent CS.

This investigation has led to the preparation of agent CS slurries containing up to 60% of the agent by weight. Several of the experimental slurries were evaluated by CRDL in explosive dissemination devices with encouraging results.

It is the intent of this working paper to present the results of CAL's slurry investigation up to 31 December 1964 under Contract DA 18-108-CML 6628(A), Project CHORD.

III. TECHNICAL DISCUSSION

Fundamental to the composition of all practical slurries are the three classes of constituents which usually coexist. The solid, or disperse, phase; the liquid, or continuous phase; and a dispersant (which can be a single chemical specie or a mixture). In the particular instance at hand, there can obviously, be no choice as to the solid, since it is a specific agent which is to be suspended. The continuous phase is chosen on the basis of long-term compatibility with the agent, both chemical (decomposition) and physical (crystal growth), as well as desired properties of volatility and viscosity, as far as obtainable. The compound, or mixture referred to as the dispersant is, therefore, the area of principal investigation in a study of slurry preparation and performance. The first ingredient of a typical dispersant mixture is a chemical compound referred to as a surface active agent (or surfactant) having a molecule characterized by the presence of regions of different affinities, one nonpolar or lipophilic and one polar or hydrophilic.

A. HYDROPHILE/LIPOPHILE BALANCE (HLB)

Important to the properties of any ultimate dispersion combining the three ingredients is the ability of the surfactant to match the essentially polar surface of the agent to the relatively nonpolar solvent. This ratio of the two functionalities of the surfactant is known as the hydrophile/lipophile balance. This property is expressed by a scale from 0 to 20, with 0 being entirely nonpolar and 20 being entirely polar; the intermediate points are a weight ratio of the hydrophillic and lipophillic portions of the molecule. In addition to HLB, the chemical type and concentration of the optimum wetting agent must be determined. However, it can be shown that, among all chemical families, the optimum surfactant of each type will have the same HLB· thus, determination of the proper HLB need only be made once, and chemical type need only be evaluated at the chosen optimum HLB. To evaluate this parameter, a set of slurries was prepared at 40% solids (by weight) with an mmd of about 2 microns (obtained by wet ball milling), and having a series

of HLB values from 1 to 15 (each with 1% surfactant based on weight of disperse phase). When viscosities of the resultant slurries were plotted (at two shear rates), the curves shown in Figure 1 were obtained, showing a definite maximum in viscosity (at all shear rates considered) at about HLB 8.5 and a slight minimum at about HLB 14.

The situation at HLB 8.5 may be considered as the point of maximum coupling between particle surface and carrier liquid which should exhibit, in addition to maximum viscosity, minimum settling (observed) and minimum interfacial slippage, and should generally behave as though the solid were a part of the liquid. The point at about HLB 14 should exhibit the antithesis of these properties, minimum viscosity (observed), maximum settling (observed), and maximum interfacial slippage.

B. SURFACTANT LEVEL

Another critical parameter of dispersion properties is surfactant level. When an identical set of slurries prepared at HLB 8.5 solids at 1%, 2%, and 5% surfactant (by weight of disperse phase), the rheological curves shown in Figure 2 are exhibited.

Another implication of surfactant level is that the ease of generation of new surface (particle size reduction) should be dependent upon the ability of the system to supply surfactant to the new surface as it is formed. In fact, when the samples in the preceding graph were ball milled under identical conditions for the same period, the slurries were as shown in the photomicrographs (Figure 3).

However, it should be noted that, beyond the concentration required to satisfy the total surface, additional surfactant goes into micelle formation of no particular utility.

C. LIQUID CHOICE

As previously mentioned, the criteria of liquid choice are physical and chemical compatibility with the desired agent and those physical properties of the liquid which may pertain to dissemination. The initial

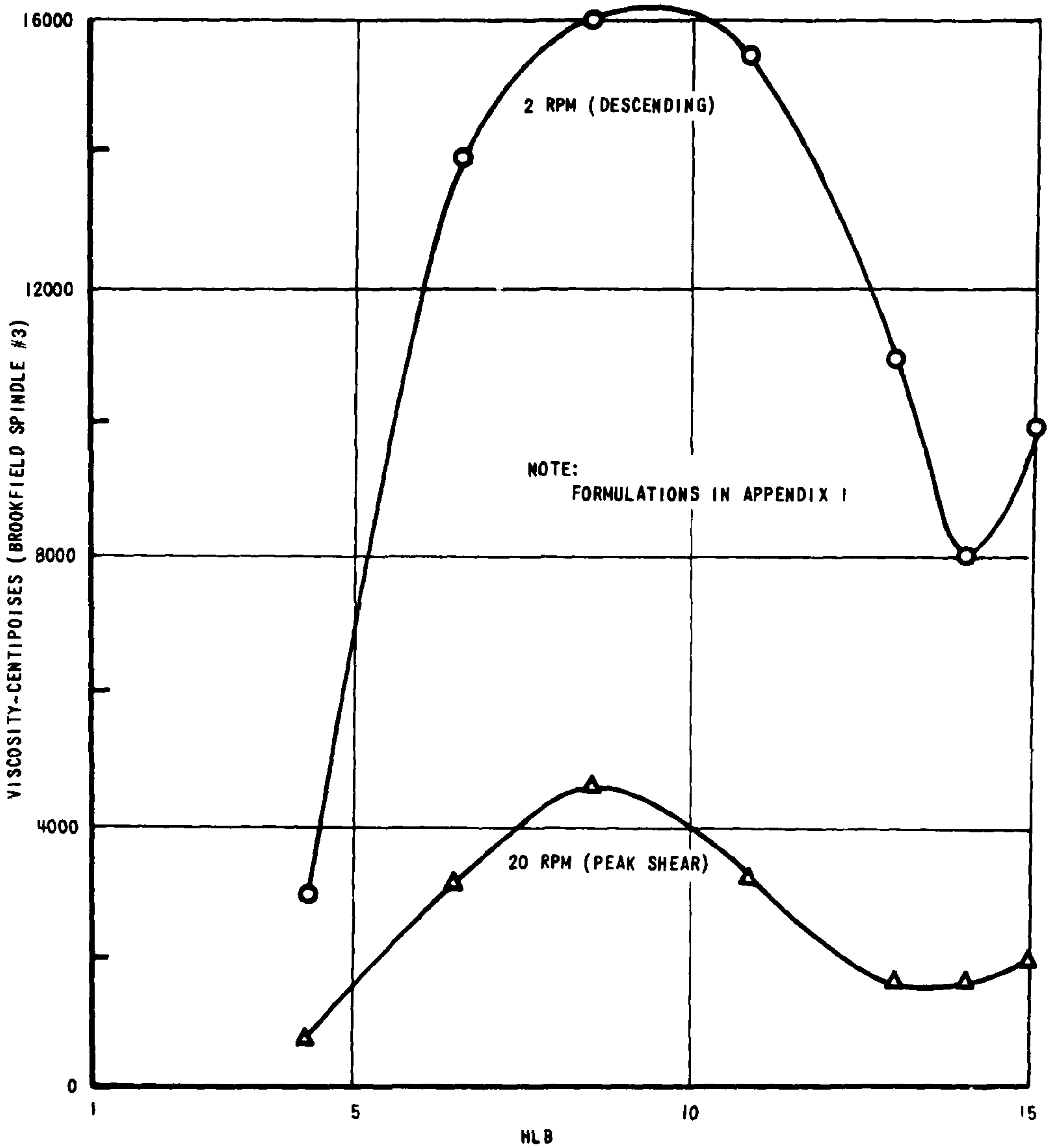


Figure I EFFECT OF HLB ON RHEOLOGY 40% AGENT CS IN CYCLOHEXANE

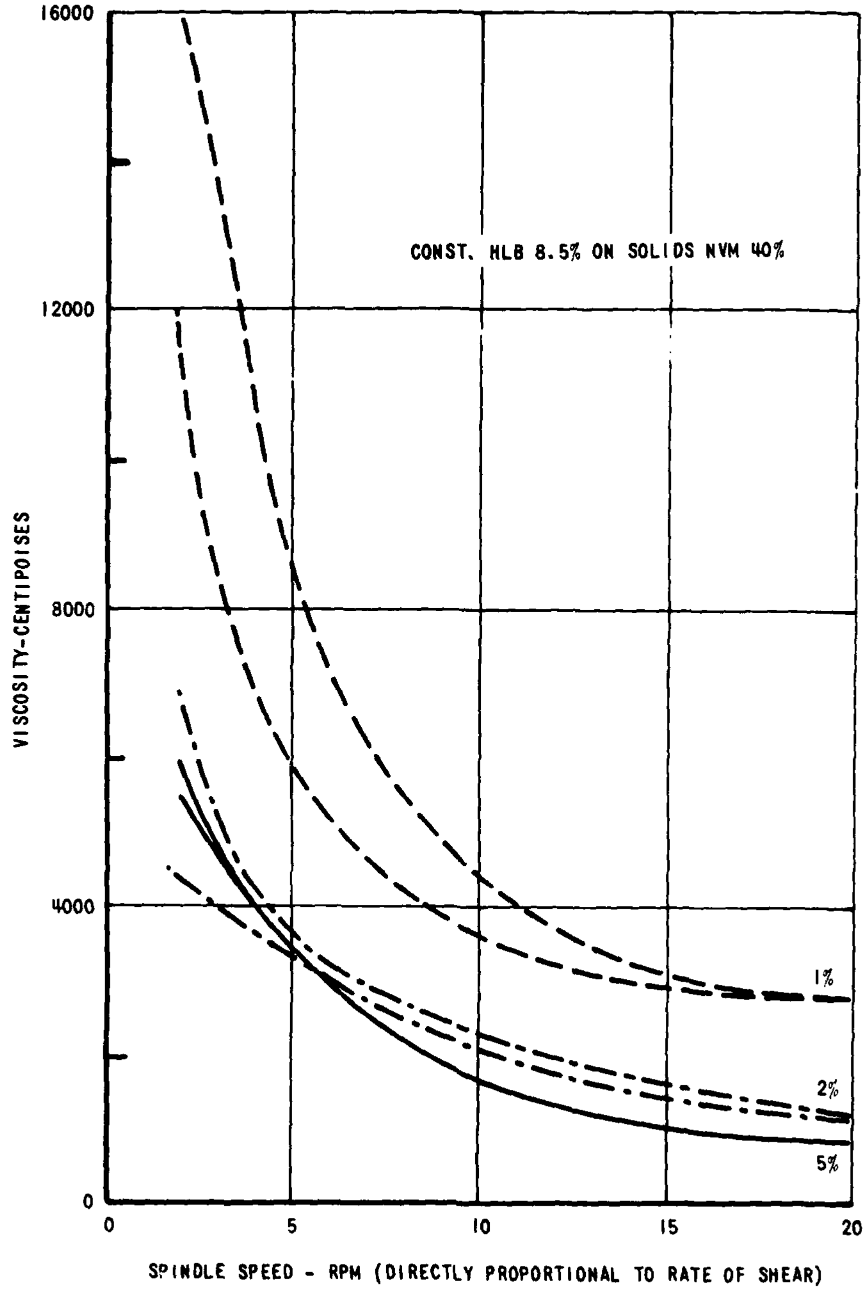
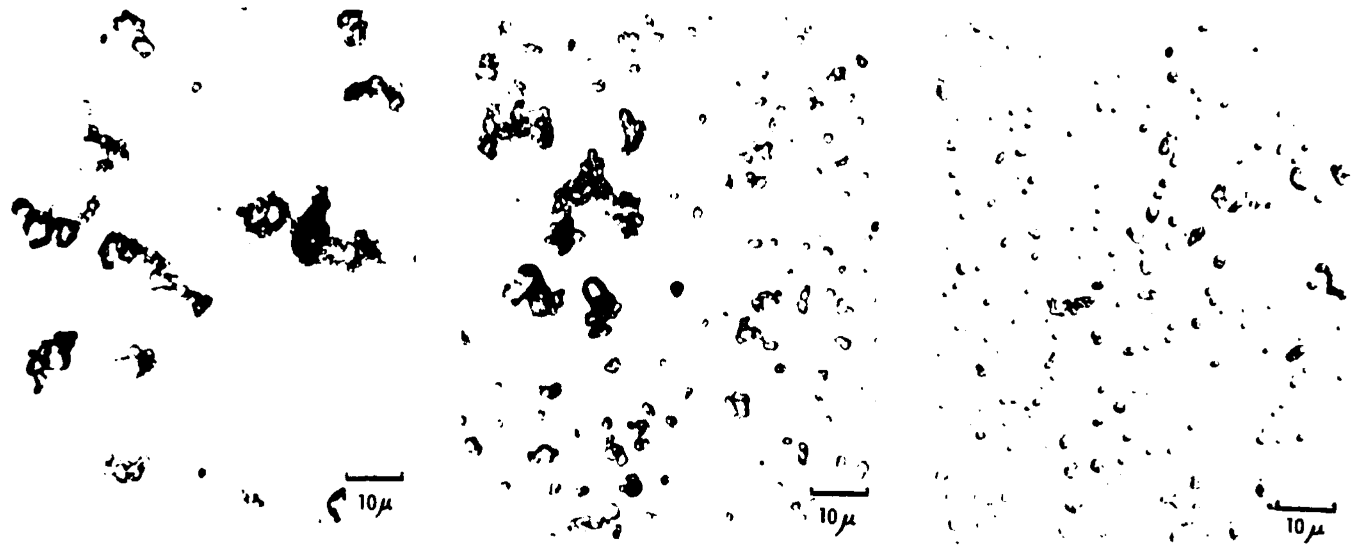


FIGURE 2 EFFECT OF WETTING AGENT CONCENTRATION ON RHEOLOGY



1% SURFACTANT AT HLB 8.5

2% SURFACTANT AT HLB 8.5

5% SURFACTANT AT HLB 8.5

3651

Figure 3 EFFECT OF SURFACTANT CONCENTRATION ON GRINDING EFFICIENCY 40% AGENT CS IN CYCLOHEXANE

approach to chemical compatibility suggested the choice of a paraffin hydrocarbon. The choice was further restricted for handling ease to a room temperature liquid and, for apparently desirable dissemination properties, to a relatively volatile liquid. After evaluating the hydrocarbons of acceptable volatility, cyclohexane was chosen as the carrier liquid, since it showed the least crystal growth in a limited test series. This compound has subsequently proved satisfactory from both dispersion and dissemination standpoints. Resistance to crystal growth on prolonged storage has been outstanding[1] as shown in Figure 4.

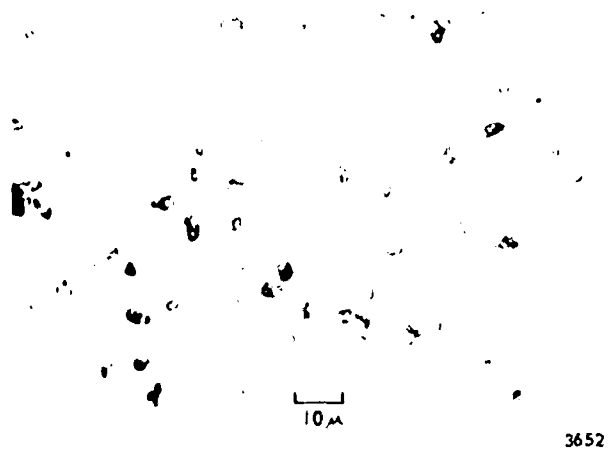
A number of early batches are now approaching one year in age with a similar lack of any visable crystal enlargement.

D. PROTECTIVE COLLOID

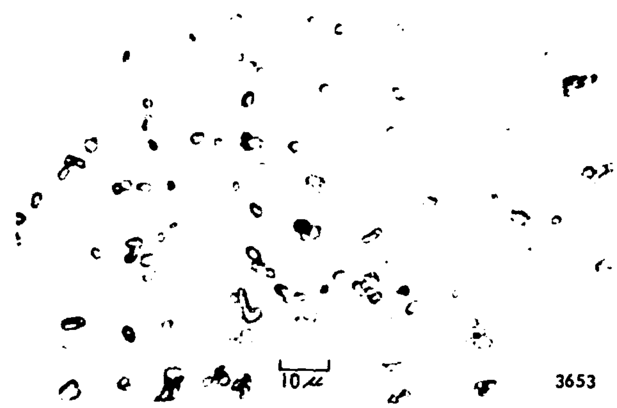
The use of a protective colloid as a portion of the dispersant system was also briefly evaluated. Protective colloids are frequent ingredients of industrial slurries (plastisols, paints, and various edible products, etc.) where they serve two purposes.

- They retard crystal growth, cementation, agglomeration, floculation, and related phenomena by interposing a physical barrier to the contact of particles of the disperse phase.
- They increase liquid mobility and decrease thixotropy by a somewhat obscure phenomenon thought to involve the internal "lubrication" of the dispersion.

[1]It might be well at this juncture to relate a pitfall. Early work was done quite successfully with technical grade cyclohexane with no apparant crystal enlargement. A sudden reversal of performance in this regard with severe crystal growth was traced to the use of a new batch of technical grade cyclohexane. At that point, the use of C. P. grade cyclohexane was begun and has continued with no further difficulty being experienced.



PHOTOMICROGRAPH OF FRESHLY PREPARED CS42-3 SLURRY



PHOTOMICROGRAPH OF 1 MONTH OLD CS42-3 SLURRY

Figure 4 CRYSTAL STABILITY

A typical protective colloid effect, shown in Figure 5, shows the rheological curves for two slurries, identical except for the inclusion of 1% soya lecithin in one. It will be noted that the viscosity is significantly lower and that thixotropy (indicated by "hysteresis" in the shear rate/viscosity curve) is essentially absent.

E. CONCENTRATION

One of the fundamental purposes of the slurry investigation is the preparation of agent CS slurries which contain high percentages of the agent. Of particular significance is the fact that slurry techniques allow greater volumetric packing of the agent than pressure packing of the dry agent.

The O.R.G. "Technical Reference Handbook" gives a value of 0.255 to 0.403, depending upon compaction pressure, as the bulk density for agent CS. Other sources have indicated a slightly higher upper limit. Even a 40% slurry, however, which was chosen for most of the agent CS slurry investigation to maximize dispersant effects, represents a packing density of 0.390 and, a 60% slurry which has been prepared (see Appendix I) has an effective packing density of 0.68. These densities are based on agent alone and do not include the weight of the carrier liquid which shares the available volume.

F. DISSEMINATION

Samples of representative slurries were used by CRDL in an explosive dissemination test series. Although detailed results are not available for publication at this time, it was found that the HLB 14 slurry showed the greatest dissemination efficiency. Accordingly, additional tests were conducted with slurries of this HLB value under a subcontract to the Illinois Institute of Technology Research Institute (IITRI). Figure 6 is a plot of the settling curve for tests conducted with an S-2 explosive dissemination device holding 4.8 grams of agent CS in the form of a 40% slurry at HLB 14 (see Appendix I for formulation). This dissemination technique seems to offer a very significant advantage over the explosive dissemination of dry pressed agent CS both from the standpoint of percent airborne on the basis of original agent weight and the superior packing density as previously discussed.

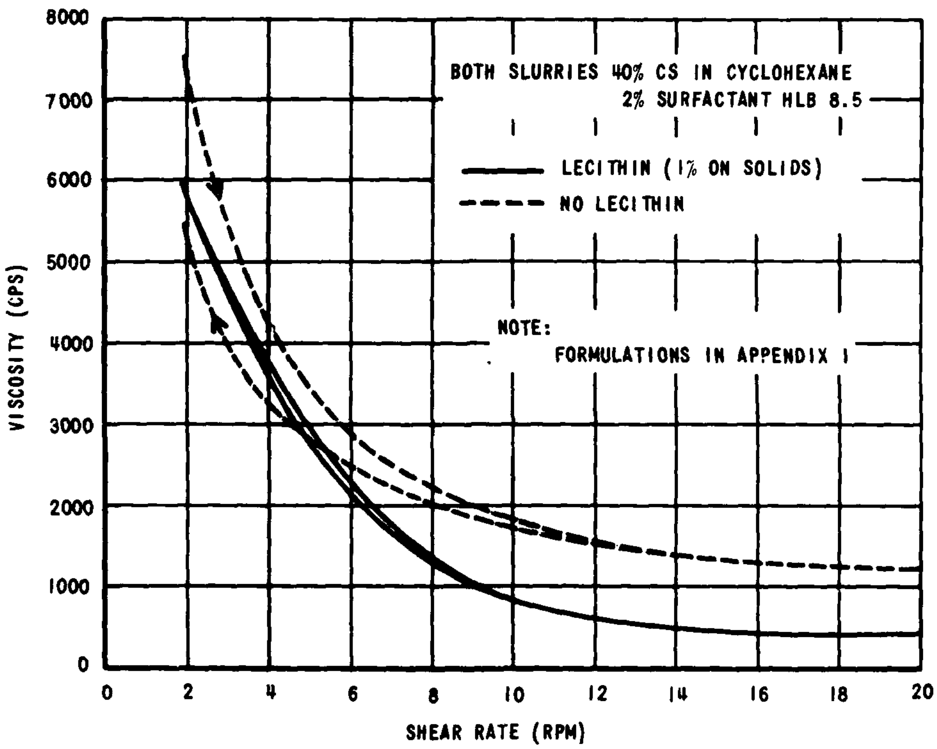


Figure 5 EFFECT OF PROTECTIVE COLLOID

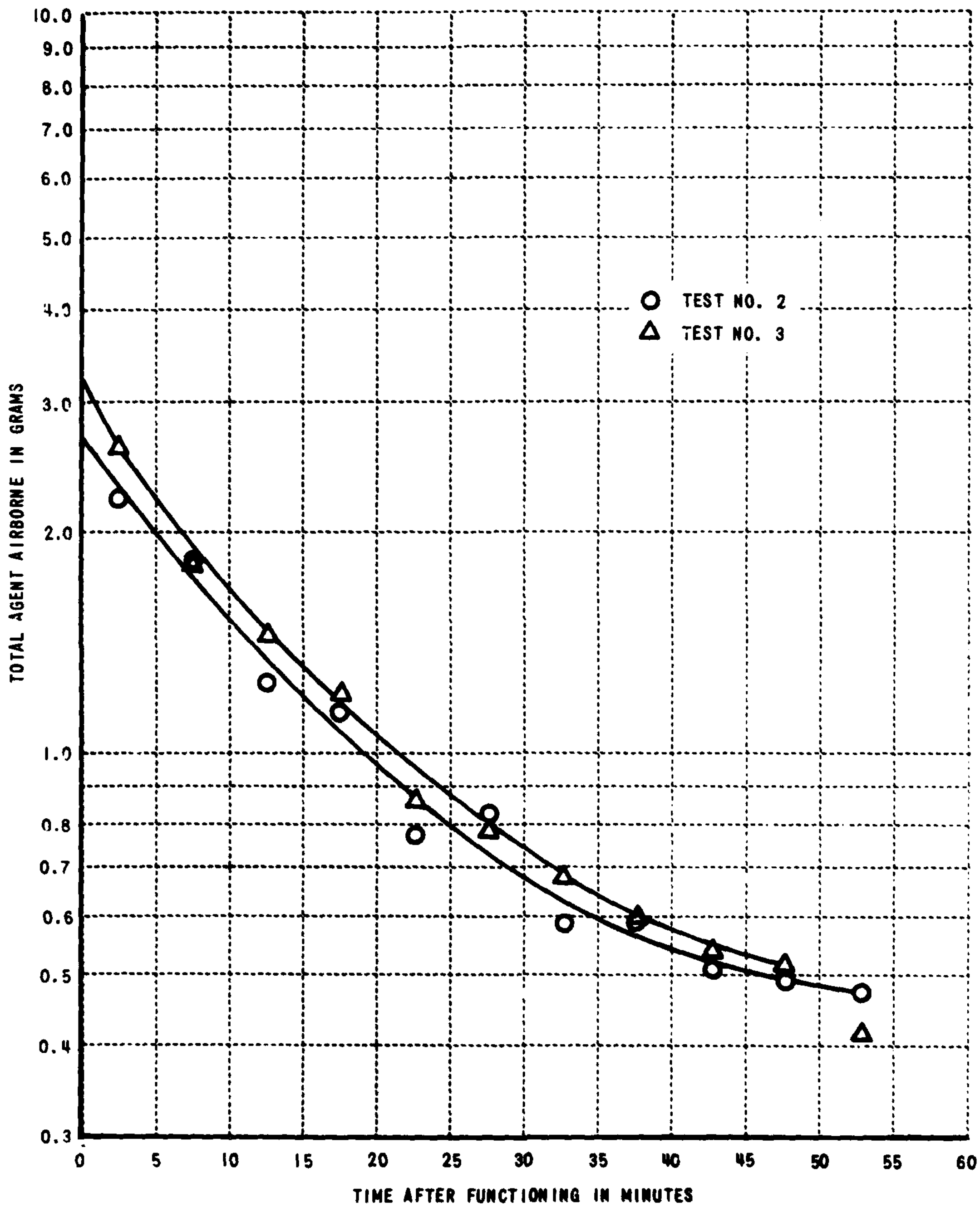


Figure 6 SETTLING CURVE FOR S2 EXPLOSIVE DISSEMINATION DEVICE WITH 40% SLURRY

An additional dissemination technique was also explored in the IITRI test series. This approach, called slurry superheat, involved the heating of an enclosed volume of slurry until the superheat caused the vapor pressure of the cyclohexane to exceed the burst pressure of a rupture diaphragm which constituted one wall of the test fixture. The diaphragm then burst, allowing the internal cavitation caused by the flash evaporated cyclohexane to cause atomization. This technique showed little or no potential for the generation of an inhalable aerosol, producing particles in the form of "snowflakes" of 50 to 150 microns diameter. Accordingly, investigation of this approach has been suspended.

It is anticipated that studies will be conducted into other dissemination techniques; notably - high-pressure, single-fluid nozzles and the velocity generator.

IV. CONCLUSIONS

During the conduct of this study, slurries of agent CS have been prepared which show a wide variety of rheological properties. In addition, techniques have been pursued which offer considerable promise in the preparation of slurries not only of agent CS but of a wide variety of solid agents in an equally wide variety of carrier liquids.

Explosive dissemination studies with dispersions prepared under this program have been conducted by CRDL. These studies have shown encouraging results with the indication that the explosive dissemination technique, desirable because it produces a volume source, may offer yields previously unobtainable with solid chemical agents.

The appendices to this working paper include the formulations for slurries representative of most of the techniques and characteristics discussed herein as well as a description of the ingredients used in these formulations.

APPENDIX I

TYPICAL SLURRY FORMULATIONS

40% slurry at HLB 4.3 1% surfactant

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	298 grams
Span 80	2 grams

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a*	850 centipoises
	b	5000 centipoises
settling	c	16%

---

*Footnotes to Characteristics in Appendix I

a Brookfield #3 spindle, 20 RPM, aged 1 week

b Brookfield #3 spindle, 2 RPM, aged 1 week

c Volume % clear supernatant liquid after 30 days undisturbed settling

40% slurry at HLB 6.5 1% surfactant

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	298 grams
Span 80	1.6 grams
Tween 80	0.4 gram

Ball mill 2 μ mmd (approx)

Characteristics:

viscosity	a	3200 centipoises
	b	14,000 centipoises
settling	c	0%

40% slurry at HLB 8.5 1% surfactant

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	298 grams
Span 80	1.2 grams
Tween 80	0.8 gram

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a	4600 centipoises
	b	16,000 centipoises
settling	c	0%

40% slurry at HLB 10.8 1% surfactant

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	298 grams
Span 80	0.8 gram
Tween 80	1.2 grams

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a	3,250 centipoises
	b	15,500 centipoises
settling	c	0%

40% slurry at HLB 13 1% surfactant

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	298 grams
Span 80	0.4 gram
Tween 80	1.6 grams

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a	1,700 centipoises
	b	11,000 centipoises
settling	c	1-2%

40% slurry at HLB 14.0 1% surfactant

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	298 grams
Span 80	0.2 gram
Tween 80	1.8 grams

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a	1,050 CPS
	b	8,000
settling	c	4%

40% slurry at HLB 15.0 1% surfactant

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	298 grams
Tween 80	2.0 grams

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a	2,050 centipoises
	b	10,000 centipoises
settling	c	0%

40% slurry at HLB 8.5 2% surfactant 1% protective colloid

(Low viscosity slurry)

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	294 grams
Span 80	2.4 grams
Tween 80	1.6 grams
Soya Lecithin	2.0 grams

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a	250 centipoises
	b	800 centipoises
settling	c	12%

60% slurry at HLB 8.5 2% surfactant 1% protective colloid

CS (micropulverized)	200 grams
cyclohexane C.P. or spectro	137 grams
Span 80	2.4
Tween 80	1.6
Soya Lecithin	2.0

Ball mill to 2 μ mmd (approx)

Characteristics:

viscosity	a, b	Pourable when freshly agitated but beyond range of available viscosimeter
settling	c	1%

APPENDIX II

TABLE OF CONSTITUENTS USED IN SLURRY FORMULATION SHOWN IN APPENDIX I

CS chemical agent as furnished by CRDL

Cyclohexane.

Flammable liquid. Solvent odor. Density 0.7781 . m + 6.47°C. b_{760} 80.7°C. n_D^{20} 1.4264. Flash point - 18°. Flammability limits in air 1.3 - 8.4%v/v. Lethal concentration for mice; 20,000 ppm in air for continuous exposure (reference: Merck Index seventh edition)

Span 80	Atlas Chemical Co. surfactant, a sorbitan monooleate with HLB of 4.3
Tween 80	Atlas Chemical Co. surfactant, a polysorbate with HLB of 15.0
Soya Lecithin	A protective colloid, pourable, thick fluid, with a density of 1.0305

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